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⑰ Applicant: W.R. Grace & Co.-Conn. (a
Connecticut corp.)
Grace Plaza 1114 Avenue of the Americas
New York New York 10036(US)

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⑰ Inventor: Vu, Cung
10971 Harmel Drive
Columbia, MD 21044(US)

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⑰ Representative: UEXKÜLL & STOLBERG
Patentanwälte
Beselerstrasse 4
D-2000 Hamburg 52(DE)

⑯ Castor oil based polyurethane for bridge decking and related applications.

⑰ Novel polyurethane formulations especially useful as membranes for the protection of bridge deckings. The polyurethane is prepared by mixing two components, A and B. Component A comprises castor oil modified with a ketone-formaldehyde condensate and also preferably contains an elastomer. Component B is a modified MDI, being a mixture of diphenylmethane diisocyanate and its reaction product with a low molecular weight poly-(oxyalkylene).

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CASTOR OIL BASED POLYURETHANE FOR BRIDGE DECKINGS AND RELATED APPLICATIONS

RELATED APPLICATIONS

5 Copending applications having U.S. Serial No. 101,215, filed September 25, 1987, and U.S. Serial No. 141,452, filed January 7, 1988, and U.S. Serial No. 209,406 filed May 19, 1988 also disclose polyurethane resins used for the purposes related to those described herein.

FIELD OF THE INVENTION

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The invention relates to polyurethane coatings used for the protection of exterior surfaces, especially concrete surfaces.

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BRIEF SUMMARY OF THE INVENTION

20 A novel polyurethane resin is applied to exterior surfaces, especially concrete surfaces subject to stress due to vehicular traffic, weather, temperature-induced dimensional changes, and the like. This resin is especially useful as a coating for concrete bridge deckings where asphalt is to be laid on the decking. The resin is applied as a mixture of two components, viz., (A) a polyol component and (B) a modified MDI (diisocyanate) component.

25 Component A consists essentially of (i) modified castor oil plus (ii) optionally an elastomer. Component B is a mixture of MDI with a prepolymer comprising the reaction product of MDI and an alkylene oxide. Either Component A or B may include a polyurethane catalyst.

BACKGROUND OF THE INVENTION

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Concrete bridge deckings are commonly coated with a protective layer of asphalt (up to 15 cm thick), uniformly spread under heavy rolling equipment, which may weigh 10 metric tons or more. This asphalt layer is exposed to extremes of weather throughout the year, and will eventually develop cracks, some so small as to be practically invisible, others much larger. All are harmful, in that they permit liquid water to penetrate down to the concrete surface, where it freezes in winter and causes sizable portions of the asphalt layer to spall away. These adverse factors (freeze-shattering, traffic impact, chloride disintegration from de-icing salt, etc.) result in serious damage to the concrete traffic surface and eventually require major repairs.

35 Aside from asphalt-coated concrete surfaces, bridge concrete in the form of superstructure, parapets, crash barriers, etc., is also subject to attack, viz., from air- or moisture-borne industrial chemicals; spattered de-icing salt; and carbonation, i.e., gradual penetration of atmospheric carbon dioxide which then reacts with the alkaline materials in the concrete and attacks reinforcement in the concrete.

40 To inhibit the aforesaid destruction, it is conventional in concrete bridge construction and maintenance to apply a bridge deck membrane (BDM) to the concrete surface before laying down asphalt. Several BDM's are available. Polyurethane has been tried.

45 A BDM should meet a number of technical and economic criteria. It should:

(1) be impermeable to liquid water from above, yet be sufficiently permeable to permit small amounts of water vapor to escape from the concrete substrate;

50 (2) be solventless;

(3) be easily applied, preferably sprayable;

(4) have good adhesion to concrete;

(5) have low chloride penetration;

(6) be stable to concrete alkali;

(7) be stable under conditions of asphalt application - hard, but not brittle, yet be sufficiently flexible to cope with dimensional changes generated by temperature differentials and bridge movements; be able to

tolerate application of asphalt at 170 °C under a 10-ton roll;

(8) provide superior adhesion of asphalt as applied to the BDM;

(9) be resistant to asphalt migration (i.e., tendency of low molecular weight hydrocarbons in asphalt to migrate into the BDM, weakening and/or destroying it).

5 (10) have competitive raw material costs;

(11) not discolor concrete;

(12) have prolonged life on exposed surfaces (e.g., vertical surfaces and other surfaces not asphalt-coated);

(13) be tough enough within a reasonable time for construction crews to walk on it.

10

Prior Art

15 An undated technical brochure entitled "Desmophen", available from Mobay Chemical Co., describes "Desmophen"® as a "branched polyalcohol with ether and ester groups" which is suitable for the production of coating compositions. In particular, the brochure discloses that Desmophen® can be reacted with isocyanates (not defined) to make polyurethane coatings for concrete and that the coating formulation must include molecular sieve zeolites "for thorough drying" (p. 12). The coating may also include fillers.

20 The coating is said to be hard and moisture resistant. There is no teaching of added elastomers. Prior to use on concrete, a primer is applied to the concrete (p. 13). The polyurethane coating may be applied to cast asphalt floorings and to steel and "bridge structures" (p. 14). Our analyses indicate that "Desmophen" contains castor oil, cyclohexanone formaldehyde condensate, and a small amount of toluene.

Castor oil is known as a polyol reactant with diisocyanates to form urethanes. Ency. Pol. Sci. and Techn. 3, 25 (1965).

25 In a brochure entitled "Bayer Engineering Polymers" (apparently dated November, 1985), Bayer UK Limited offers commercially a polyurethane made from a polyether polyol (Component A) and a modified MDI (Component B). No further disclosure of the composition is given. The two components are mixed at the site, e.g., by spraying, on bridge decking or other concrete surface. The applied resin is said to cure 30 tack-free in a few minutes and can be walked on in 20-30 minutes.

In a technical brochure on "352-Oldopren-S" (apparently dated March, 1983), Buesing & Fasch GmbH & Co. of Oldenburg, Germany, describe an MDI-based 2-component, polyurethane that provides an elastic film, useful (under asphalt) on road- and bridge-concrete surfaces.

35 R. I. Frascoia describes the use of four polyurethane membranes in bridge deck systems in an article, "Field Performance of Experimental Bridge Deck Membrane Systems in Vermont", Transportation Research Record, pp. 57-65 (1984). Three of the polyurethanes were asphalt-modified, but formulations are not otherwise given. The bond between bituminous pavement and membrane was rated "Poor", but overall performance was rated "Fair to Good".

40 Use of an "asphalt-extended urethane membrane" is described in an article by A. L. Meader, Jr. et al, "Development of a Cold-Poured Bridge Deck Membrane System", ASTM Special Technical Publications N 629, pp. 164-177 (1976).

45 For a good review article, especially for UK practice, see M. D. McDonald, "Concrete Bridge Deck Waterproofing Systems: In Highways and Road Construction, pp. 26-30 (August 1973). According to the article, polyurethane is blended with pitch to improve low-temperature flexibility and to reduce raw material costs; the membrane may need an epoxy primer (on concrete) and may need a surface protective layer before rolling on the final asphalt coating. "Cracking" and "chisel" tests are described.

50 An undated brochure, "Poly bd® Resins in Urethane Elastomers", released by Arco Chemical Co., discloses dihydroxyl-terminated polybutadiene and its reaction with aromatic diisocyanates. Page 3 of the brochure discloses a polybutadiene, "R-45HT", with structural formula, indicating the molecular weight to be about 2,800. (The use of this polybutadiene is illustrated in Examples 1 and 2 below.)

55 In a technical bulletin, "Hycar Reactive Liquid Polymers" released by B.F. Goodrich Co. (apparently dated March, 1981), Hycar polymer is described as an acrylonitrile-based diol that can be reacted with MDI to provide low temperature flexibility and chemical resistance.

U. S. Patent 4,608,203 (1987) discloses a polyurethane coating for bridge concrete, prepared from 56 polyols and MDI. The polyols can be a mixture of poly(propylene oxide) (col. 1, line 65), glycerine (col. 2, line 3), and acrylonitrile-butadiene copolymer (col. 2, line 35).

U. S. Patent 4,689,268 (1987) discloses a 3-layer laminate on concrete, viz., epoxy resin plus filler, a bonding agent, and a polyurethane.

U. S. Patent 4,559,239 (1985) describes a 2-component (polyol-MDI) polyurethane applicable to concrete.

U. S. Patent 3,725,355 discloses glycerine, polyether polyol, and an isocyanate prepolymer. The polyol can be a triol and must have a molecular weight of at least 2,000.

5 U. S. Patent 4,507,338 (1985) describes a 2-component ("A" and "B") polyurethane, sprayable as a roof coating. "A" is (e.g.) a liquid modified MDI plus a chlorinated paraffin; "B" comprises (e.g.) a polypropylene glycol, 1,4-butanediol, and dibutyltin dilaurate catalyst.

U.S. Patent 4,567,230 discloses use of molecular sieves as moisture absorbers in polyurethane resins.

10 U.K. Patent 1,182,884, Gruber and Fehlbier (1970) describes treatment of castor oil with cyclohexanone formaldehyde condensate, thereby providing modified castor oil as used herein. Reaction of the modified castor oil with MDI to make a polyurethane resin is also disclosed.

Canadian Patent 927,642 (1973) describes applying a polyurethane foam directly to a roadbed (not to concrete), followed by a bitumen layer on the polyurethane foam.

15 The combination of MDI and poly(propylene oxide) triol is disclosed, e.g., in U. S. Patents 3,515,899, 4,532,318, and 4,604,445.

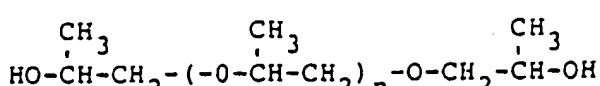
Description of Certain Components

20 Modified Castor Oil

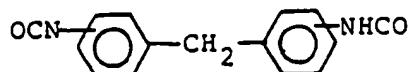
Castor oil is a well-known commercial product. It contains (depending on source) about 85 - 90% ricinoleic triglyceride, with small amounts of the glycerides of other fatty acids, e.g., oleic and linoleic. 25 Solvent-extracted castor oil may contain small amounts of solvent, e.g., 1% toluene. The castor oil used in this invention can be any of those commercially available and is treated with cyclohexanone-formaldehyde condensate as described in U.K. Patent 1,182,884, above cited. In the examples herein, the amount of cyclohexanone condensate is about 3% of the total weight of castor oil and condensate. In lieu of cyclohexanone-formaldehyde condensate, other ketone-formaldehyde polymers are useful, and in varying amounts, as described in U.K. 1,182,884. Modified castor oil as described herein is commercially available.

Modified MDI

35 Modified MDI as used herein can be made by reacting together diphenylmethane 4,4'- or 2,4'-diisocyanate (MDI) with a poly(oxypropylene) glycol of the formula:



45 The value of n lies, approximately, between 0 and 3 indicating that the material is a mixture, probably with small amounts of higher and lower molecular weight polymers of the same genus. In the main reaction the MDI end-caps both ends of the poly(oxypropylene) glycol. The prepolymer thus formed may also contain small amounts of other products of the reaction, containing isocyanate and/or hydroxyl groups. The prepolymer is typically $\text{K}-\text{O}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_m-\text{K}$ where K is



55 and m is about 2-5. In general, this material may be described as an MDI/polyisocyanate material comprising about 45-50 weight % MDI with the balance being the described prepolymer, i.e., with some prepolymer molecules being relatively small and others larger (depending generally on the amount of capped polyoxypropylene), but with the averages being substantially as above enumerated.

Instead of poly(oxypropylene) glycol, oxyethylene and oxybutylene homologs can be used with similar

results.

Whereas MDI is a solid, and is very difficult to handle in spray apparatus, the above described MDI/polyisocyanate prepolymer is a homogeneous liquid and is readily sprayed.

5

Elastomers

10 Hycar 1300 X 17 is a long chain acrylonitrile-butadiene hydroxyl-terminated diol (copolymer with 17% acrylonitrile) available from BFGoodrich Co., Cleveland, Ohio. Weight average molecular weight is about 4,000, viscosity, 140,000 cp; hydroxyl number, 25 mg KOH/g; residual carboxyl acid number, 3.9.

Poly bd^(R) is a liquid dihydroxy-terminated polybutadiene, molecular weight about 2,800, available from Arco Chemical Co., as above described.

15

DETAILED DESCRIPTION OF THE INVENTION

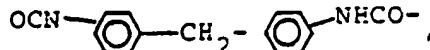
20 My polyurethane resin is formed basically of two components identified, for the sake of brevity, as (A) and (B). (A) comprises polyols, and (B) comprises polyisocyanate.

(A) consists essentially of (i) modified castor oil as above and, optionally, (ii) an elastomer preferably, but not necessarily, with functional groups such as hydroxyl, amino, active hydrogen, etc., capable of reacting with polyisocyanate, suitably an elastomeric diol.

25 The elastomer can be one of the following: natural rubber, epoxidized natural rubber, ethylene-propylene rubber, nitrile rubber, styrene-butadiene rubber, acrylic elastomers, butyl rubber, chlorosulfonated polyethylene, neoprene, polybutadiene, polyisoprene, and the like. I prefer polybutadiene (such as Poly bd^(R) 45HT, as above described) or an acrylonitrile-butadiene copolymer (such as Hycar 1300 X 17, as above described).

30 The elastomer functions in at least two ways. First, it provides flexibility to the polyurethane membrane in a manner that permits the membrane to flex under the continuous flow of heavy traffic, month after month, without cracking. Secondly, it provides flexibility which is maintained even at sub-zero temperatures.

35 Component B is a modified MDI, viz., a mixture of MDI with a prepolymer made by reacting MDI with a lower alkylene oxide (2-4 carbons). MDI is diphenylmethane diisocyanate. It is available commercially, e.g., as a mixture of isomers, typically mixtures comprising mostly the 4,4'-isomer, with the balance of the 2,2'-isomer. A 98% 4,4'-, 2% 2,2'-isomer mixture is available from Dow Chemical Co. as PAPI-94, and many other MDI isomer mixtures are available and useful in my invention. For example, MDI (as the 2,4'- or 4,4'-isomer, or a mixture) can be reacted with an alkylene oxide to make an MDI prepolymer. As the alkylene oxide I prefer ethylene or propylene oxide. Especially useful as Component B is a modified MDI containing about 45-50 weight % 4,4'- and/or 2,4'-diphenylmethane, with the balance to make 100% being a 40 polyisocyanate prepolymer of the structure K-O-(CH₂CH[CH₃]O)_m-K, where K is



45

and m is about 2-5. Prepolymer polyisocyanates of this type are available as Mondur XP-744 (Mobay), Isonate 181 (Dow Chemical Co.), etc.

50

Catalyst/No Catalyst

55 My formulations can be used with or without a catalyst, depending on the method of the application. If the formulation is sprayed or otherwise applied in such manner that the two components are admixed at the point of application, a catalyst may be desirable to ensure quick setting, i.e., dry-to-touch within minutes. On the other hand, where the components are mixed in a container, and the container is required to supply the complete polyurethane formulation over a period of time (say, 30 minutes), then not only is a catalyst inadvisable, but an inhibitor may actually be necessary for the desired extended pot life. A number of

polyurethane inhibitors are known, including: organic and inorganic acids, such as benzoyl chloride, p-toluene sulfonic acid, formic acid, acetic acid, benzoic acid, phosphoric acid, hydrochloric acid, and the like.

When an inhibitor is used, it is suitably about 0.01-1.0 weight % of the overall polyurethane mix.

A catalyst is recommended for spraying operations or where the formulation is to be applied to concrete immediately on mixing. For this purpose, substantially any of the conventional polyurethane catalysts (and combinations) can be used.

These catalysts include:

Tertiary amines:

- 5 Triethylene diamine
- 10 N-methyl morpholine
- N-ethyl morpholine
- Diethyl ethanolamine
- 1-methyl-4-dimethylamino ethyl piperazine
- 3-methoxy-N-dimethyl propyl amine
- 15 N-dimethyl-N'-methyl isopropyl propylene diamine
- N,N-diethyl-3-diethyl amino propylamine
- N,N-dimethyl benzyl amine
- Dicyclohexylmethylamine
- 2,4,6-tris dimethylaminomethylphenol
- 20 N,N-dimethyl cyclohexylamine
- Triethylamine
- Tri-n-butylamine
- 1,8-diaza-bichloro[5,4,0]-undecene-7
- N-methyl diethanolamine
- 25 N,N-dimethyl ethanolamine
- N,N-dimethyl cyclohexylamine
- N,N,N',N'-tetramethyl-ethylene diamine
- 1,4-diaza-bicyclo-[2,2,2]-octane
- N-methyl-N'-dimethylaminoethyl-piperazine
- 30 Bis-(N,N-diethylaminoethyl)-adipate
- N,N-diethylbenzylamine
- Pentamethyldiethylene triamine
- N,N,N',N'-tetramethyl-1,3-butanediamine
- 1,2-dimethylimidazole
- 35 2-methylimidazole
- Tin compounds:
- Stannous chloride
- Dibutyl tin di-2-ethyl hexoate
- Stannous octoate
- 40 Dibutyl tin dilaurate
- Trimethyl tin hydroxide
- Dimethyl tin dichloride
- Dibutyl tin diacetate
- Dibutyl tin oxide
- 45 Tributyl tin acetate
- Tetramethyl tin
- Dimethyl dioctyl tin
- Tin ethyl hexoate
- Tin laurate
- 50 Dibutyl tin maleate
- Dioctyl tin diacetate
- Other metal organics:
- Zinc octoate
- Phenyl mercuric propionate
- 55 Lead octoate
- Lead naphthenate
- Copper naphthenate

As to the amount of catalyst(s), the preferred amount of tertiary amine catalyst is about 0.001 - 0.5%.

based on the total weight of polyols plus polyisocyanate. When using a tin compound or other metal-containing catalyst, an equal amount is suitable. Mixtures of tertiary amines and -organo-metallics are particularly suitable as catalysts for this invention. Suitable ratios for certain components are:

5

TABLE I

	Workable Ranges Parts by Wt.	Preferred Ranges Parts by Wt.
10	Component A	
15	Modified Castor oil Elastomer Molecular sieves	about 90 to 140 about 0 to 120 0 to 50
20	Component B	about 100 to 130 about 20 to 100 about 5 to 40
25	Modified MDI	about 50 to 70
30		about 55 to 65

20 Generic and preferred embodiments of the invention include:

- (1) the novel combination of Components A and B as set forth in generic and specific formulations herein;
- (2) the processes (generic and specific) of mixing together Components A and B aforesaid;
- (3) the resins (generic and specific) resulting from (2) above;
- 25 (4) process of coating a substrate with the resins of (3) above. Substrates of particular interest are metals and concrete, e.g., bridge decking.
- (5) coated metal or concrete articles resulting from (4) above;
- (6) overall process of protecting metals or concrete bridge decking by applying the resins of (3) above to metals or concrete, as the case may be;
- 30 (7) as an article, bridge decking comprising concrete-polyurethane-asphalt laminate, the polyurethane being the resin of (3) above.

Mixing and Application

35

For small batches, such as might be needed for minor repair work to decks and parapets, the two Components A and B can be mixed in an open container at room temperature, and the mixture can then be spread on the concrete surface. To extend pot life, it may be desirable to eliminate the catalyst, or even to use an inhibitor. For general large scale work (and the resin is designed for this) a conventional two-liquid air spray gun is recommended for best results.

40

Application to the deck surface is suitably made at ambient temperature, preferably above freezing. The coated substrate is rapidly tack-free and cures at ambient temperature.

45

It is preferred that the resin be applied to a dry surface. However, some dampness can be tolerated. Following conventional practice, I prefer to spray the surface with a primer.

50

I prefer to apply about 1 - 5 kg resin/meter² of surface. I can apply this as one, or, suitably, two or more coats. This makes a film of about 1 - 5 mm thickness. For deckings subject to extremely heavy traffic, I prefer the upper levels of these ranges.

The following examples are merely illustrative and are not to be construed in any way to limit the scope of the claimed invention.

Example 1

55

This represents a preferred embodiment of the invention. A polyurethane coating was prepared from two components, A and B, in parts by weight given as about:

Component A	Parts
Castor oil modified according to claimed invention	100.0
Polybutadiene (Poly BD)	30.0
Molecular sieve (Baylith L)	6.0
CaCO ₃	27.0
Cr ₂ O ₃	2.0
fumed silica (R-202)	1.0
dibutyl tin dilaurate (DBTDL)	0.1
DABCO LV-33 from Air Products (67% polypropylene glycol, 33% triethylene diamine)	0.3
Component B	
Polyisocyanate Prepolymer (Mobay's Mondur XP-744)	60.0

15

The ingredients listed under Component A were mixed to form Component A, which was then mixed with Component B. Reaction occurred instantaneously. The resulting polyurethane can be sprayed or doctoried onto concrete or other substrates. The coating cures within minutes. Tests show that the coating is very hard and adheres well to concrete. It has a particular advantage in that it is hydrophobic and resists reaction with moisture, thereby greatly diminishing formation of bubbles in the coating.

Example 2

25

The above ingredients were formulated and used to produce the claimed invention, except that XP-744, the polyisocyanate prepolymer used for component B, was substituted one for one in parts by weight with Isonate 181 (Dow Chemical Co.).

30

Comparison Example 1

35

For comparison purposes, several runs have also been made in which component A only comprises castor oil. However, the resulting polyurethanes were too soft for serious consideration as a BDM.

40

Fillers in the above formulations (e.g., molecular sieves and fumed silica) assist in viscosity control of the liquid polyurethane, aid in levelling the coating, and act as moisture absorbers. (See, e.g., U. S. Patent 4,567,230, supra.) The moisture comes not from the resin, but rather from the underlying concrete and from the atmosphere. Even well-cured concrete tends to release water vapor, which tends to form blisters in BDM's, especially in freshly laid membranes. The demoisturizing fillers can, however, be omitted, with acceptable results.

45

In the general case, and especially in humid conditions, molecular sieves should be added to the formulation when it is to be sprayed. The spray droplets tend to absorb atmospheric moisture, and this moisture reacts with the polyisocyanate to release carbon dioxide, which causes foaming in the membrane with consequent severe deterioration of properties in the cured membrane. Molecular sieves inhibit this foaming by absorbing moisture before it can react with the polyisocyanate component. When molecular sieves (or equivalent moisture absorber) is used, a suspending (thixotropic) agent is preferably used to maintain the molecular sieves in suspension. These materials are well known and are available commercially.

50

It is expected that the coatings of this invention will meet the following tests.

Tests derived from the British Board of Agreement(B.B.A.):

55

Water vapor permeability (similar to ASTM E-96, Method B).
 Resistance to chloride ion.
 Resistance to cracking.
 Resistance to water penetration (similar to ASTM E-96).

Resistance to chisel impact.
 Resistance to ball indentation.
 Resistance to aggregate indentation.
 Tensile bond (adhesion)

5

Test originating in laboratories outside the B.B.A.:

Asphalt migration.

10 Certain of the above tests are summarized below.
 So far as I am aware, there are no official requirements (whether at the national or state level) for polyurethane or other BDM's. However, the construction industry has come to expect certain properties, and the chemical industry has attempted to meet these expectations. Such parameters have on occasion been offered as guidelines, as distinct from requirements. In general, the tests, however, defined and 15 formulated, aim at demonstrating properties that meet practical problems of actual road use, as elsewhere delineated. Some of the tests have been developed by official agencies (e.g., the British Board of Agreement), some by the construction industry, some by the American Society for Testing Materials (ASTM), and some by suppliers of polyurethane components.

16 The following is a summary of the tests which were conducted on the claimed invention. These tests 20 were based on those found in Appendix B, Department of Transport Checks and Tests for the Approval of Waterproofing Systems for Concrete Decks to Highway Bridges, published by the British Board of Agreement, and is current as of 1987:

(1) Water vapor permeability. (Test per British Standards 3177:1959.) Permeability of water at 25°C and 75% relative humidity should not exceed 15 g/m²/day.
 25 (2) Resistance to chloride ion. Concentrated NaCl solution on upper side of membrane, distilled water on lower. After 7 days no Cl⁻ ion penetration as shown by silver nitrate added to lower container.
 (3) Resistance to cracking. Concrete slab is coated, then pressure applied incrementally at a rate of 0.2 mm/min from the other side to crack the slab. It is desirable, and a pass is bestowed, if the crack in the slab reaches 2.5 mm before fracturing the coating to create a visible 12 mm-long fracture in the coating. If 30 more than 1 crack appears in the concrete, then any cracks in the coating should be less than 25mm.
 (4) Resistance to water penetration. Samples supported on gauze are subjected to 6,010 kg/m² water pressure for 24 hours without penetration.
 (5) Resistance to chisel impact. Total of 40 impacts, at 20°C and 0°C, with a chisel weighing 1 kg, with head 20 mm wide and 90° tip angle, dropped from a height of 200 mm in guides. Aim is less than 5% punctures. The damage caused by each impact is recorded to a specific scale. Mean of all drops must be less than or equal to 3 and the % of impacts in categories 4 or 5 must be less than 5%.
 (6) Tensile bond. 150 mm square samples of coating are applied to concrete blocks, then steel plates are adhered to the coating's upper surface by using an epoxy or similar adhesive. Load required to pull the membrane from the concrete should not be less than 1,200 N (7.73 psi).
 40 (7) Resistance to indentation (ball). A 200 mm x 200 mm sample of coating was bonded to a steel plate, and then a 20 mm diameter steel ball pressed into the sample for 5 minutes at 1800 N. A further test was conducted wherein a 5 mm ball was pressed into the sample at 400 N. Penetration to the plate is determined by addition of salt solution to the indentation and attempted passage of electric current (1,000 v) therethrough. Even with replications, the polyurethane should not be penetrated. (8) The Aggregate 45 indentation test was formerly listed in the B.B.A., but is no longer used. However, the following summary is provided for historical purposes. 150 mm square sample of polyurethane on concrete slab is topped with a layer of 14-22 mm crushed granite aggregate and a load of 5,625 kg is applied for 5 minutes. The polyurethane should not be penetrated.

50 The following is a tabulation of the results achieved by the coating compositions described in the preceding Examples.

Table II

5	Test Criteria As numbered above	Details	Examples	
			#1	=2
10	#1	Moisture vapor transmission	P	P
15	#2	Resistance to chloride ions	P	P
20	#3	Resistance to cracking at 0° and 20° C.		
25		At 0° C:		
30		crack in concrete (mm) =	0.5 1.0 2.0 2.5	P P P P
35	#4	Resistance to water penetration	P	P
40	#5	Chisel impact at:		
45		0° C	1.9	2.0
50		20° C	2.5	1.8
55	#6	Tensile Bond on Concrete		
60		1 day at 25° C (psi)	16.2	21.3
65		28 days at 70° C (psi)	27.8	27.8
70	#7	Resistance to indentation	Test stopped	Test stopped
75		Condition 1: 1800N on 20 mm ball	P	P
80	#8	Condition 2: 400N on 5 mm ball	P	P
85		Aggregate indentation	P	P
90	NOTE: P = Pass; F = Fail			

Other Tests

Additional tests were conducted to illustrate other advantageous properties of the claimed invention. For instance, as mentioned earlier, membrane degradation resulting from water and chloride and alkali ions is always a concern for road materials. The following test results indicate excellent properties in this area as well.

Test	Details and Requirements	#1	#2
6	#9 Resistance to water degradation 1 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 7 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 28 days at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, %	1680 212 5.3 1710 247 0.33 1380 189 -1.4	1900 174 0.08 1840 192 0.53 1800 190 1.4
10			
15	#10 Resistance to Chloride degradation 1 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 7 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 28 days at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, %	1920 231 0.15 1690 224 -0.34 1910 199 -0.62	1850 134 0.01 1950 174 -0.38 2010 187 1.065
20			
25			
30	#11 Resistance to alkali degradation 1 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 7 day at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, % 28 days at 70 °C Tensile strength, psi Elongation, % Weight gained/loss, %	1800 236 0.08 1650 264 0.44 1910 199 -0.16	1980 172 0.19 1970 188 0.68 1880 192 1.2
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45 As illustrated above, little change in properties were experienced in the above tests after subjecting the claimed membrane to 70 °C for 1, 7 and 28 days respectively. It should be noted that by subjecting the membrane to degradation conditions for 28 days at 70 °C the membrane underwent the equivalent of at least 5 years of degradation conditions.

50 Asphalt Migration

55 A coupon is dipped with 2 mm-polyurethane coating in asphalt at 175 °C for 1 hour. After recovery of the coupon, it is determined by visual inspection whether asphalt has migrated into the polyurethane, or whether the coating is embrittled, discolored, or otherwise deteriorated. Both samples #1 and #2 passed this test with no migration.

Some of these tests point to seemingly contradictory requirements; for example, the perfect membrane should be tough and hard, permitting the overlay of hot asphalt by heavy equipment, but at the same time the membrane must be sufficiently flexible and elastic so that if the underlying concrete cracks, the

membrane will not likewise crack. Perhaps the perfect membrane does not exist. Our preferred formulations, on the other hand, are expected to meet major requirements.

Besides molecular sieves and thixotropic agents, we can also add antioxidants, reinforcing agents, plasticizers, UV stabilizers, pigments, fillers, and corrosion inhibitors, in amounts ranging from about 0.01 to 5 25% by weight of the total composition.

Percentages are by weight unless otherwise stated.

Claims

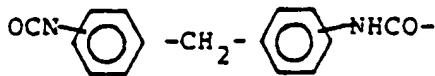
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1. Composition consisting essentially of two separate components, A and B, wherein Component A consists essentially of, in parts by weight, (i) about 90-140 parts ketone-formaldehyde modified castor oil; and (ii) about 0-120 parts an elastomer, and Component B consists essentially of about 50 -75 parts of a mixture comprising diphenylmethane diisocyanate and the reaction product of diphenylmethane diisocyanate (MDI) with an alkylene oxide of 2-4 carbons.

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2. Composition according to Claim 1, wherein Component B, comprises about 45-50 weight % 4,4'- or 2,4'-diphenylmethane and balance to make 100% of a polyisocyanate of the structure K-O-(CH₂CH₂CH₃)_m-K, wherein K is

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and m is about 2-5.

3. Composition according to Claims 1 or 2, wherein the castor oil is modified with about 3% cyclohexanone formaldehyde condensate, the elastomer is polybutadiene or an acrylonitrile-butadiene copolymer; and the weight ratio of modified castor oil: elastomer: Component B is about 90-140: 0-120: 50-75, preferably 100-130: 20-100: 55-65.

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4. Composition according to Claims 1 to 3, wherein Component A comprises at least one additive selected from the group consisting of polyurethane catalyst, polyurethane inhibitor, molecular sieves, thixotropic agents, anti-oxidants, reinforcing agents, plasticizers, UV stabilizers, pigments, fillers, and corrosion inhibitors.

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5. Composition according to Claim 4, wherein the weight ratio of modified castor oil: elastomer: Component B: additive is 90-140:0-120:50-75:0-50, preferably 100-130:20-100: 55-65:10-40.

6. Composition according to Claim 1, wherein, in parts by weight,

Component A consists essentially of :

about 100.0 parts modified castor oil,

about 30.0 parts polybutadiene

about 6.0 parts molecular sieves in castor oil, 1:1,

27.0 parts CaCO₃

2.0 parts Cr₂O₃

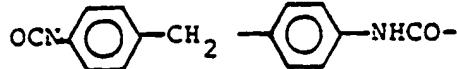
1.0 parts fumed silica

0.1 parts dibutyl tin dilaurate, and

45 0.3 parts composition comprising about 70% polypropylene glycol and about 30% triethylene diamine (DABCO)

Component B consists essentially of about 60.0 parts modified MDI, said modified MDI having the structure K-O-(CH₂CH(CH₃)_m-K, wherein K is

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55 and m is about 2-5.

7. Polyurethane resin, wherein said resin is the product obtained from the reaction of Component A and Component B as defined in Claims 1 to 8.

8. Process of forming a polyurethane resin comprising mixing together two components, A and B, as

defined in Claims 1 to 8.

9. Process of coating a substrate comprising applying thereto a resin as defined in Claim 7.
10. Process according to Claim 9, wherein the substrate is concrete or metal.
11. Process according to Claim 10, wherein the concrete is bridge decking.
- 5 12. Article comprising a substrate and a film coating adhered thereon, said film coating comprising the resin of Claim 7.
13. Article according to Claim 12, wherein the substrate is concrete or metal.
14. Article according to Claim 13, wherein the concrete substrate is bridge decking.
15. Article comprising concrete bridge decking having a layer of polyurethane resin as defined in Claim
10 7 applied thereon, and a layer of asphalt on the resin layer.

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⑰ Applicant: W.R. Grace & Co.-Conn. (a
Connecticut corp.)
Grace Plaza 1114 Avenue of the Americas
New York New York 10036(US)

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⑰ Inventor: Vu, Cung
10971 Harmel Drive
Columbia, MD 21044(US)

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⑰ Representative: UEXKÜLL & STOLBERG
Patentanwälte
Beselerstrasse 4
D-2000 Hamburg 52(DE)

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④ Castor oil based polyurethane for bridge decking and related applications.

⑤ Novel polyurethane formulations especially useful as membranes for the protection of bridge deckings. The polyurethane is prepared by mixing two components, A and B. Component A comprises castor oil modified with a ketone-formaldehyde condensate and also preferably contains an elastomer. Component B is a modified MDI, being a mixture of diphenylmethane diisocyanate and its reaction product with a low molecular weight poly(oxyalkylene).

EP 0 361 170 A3



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, Y	EP-A-0 280 981 (W.R. GRACE & CO.) * Claims 1,3,15; page 8, lines 1-11 * ---	1-15	C 08 G 18/54 C 08 G 18/80 C 08 G 18/36 C 08 G 18/72 C 09 D 175/04 E 01 D 19/08
D, Y	GB-A-1 182 884 (BAYER) * Claims 1,2; page 2, lines 29-90 * ---	1-15	
A	GB-A-1 369 334 (I.C.I.) * Claims 1-3 * -----	1	
TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
C 08 G C 09 D			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	15-01-1990	VAN PUYMBROECK M.A.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			